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A FATE CONSTANT DATA PROGRAM

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A program for compiling equilibrium and kinetic constants for predicting chemical transport and transformation in the environment is described. The fate constant data are obtained by searching the literature for reported measurements, by convening a panel of experts to postulate transformation pathways and products, by using computational techniques to estimate values, and by performing laboratory studies when measurements cannot be found or computed. Emphasis is placed throughout the program on quality control features to assure the reliability of the data.

KEY WORDS: Environmental fate data.

INTRODUCTION

Assessment of potential risk posed to humans by man-made chemicals in the environment requires the prediction of environmental concentrations of those chemicals under various scenarios. Whether mathematical models or other assessment techniques are employed, knowledge of equilibrium and kinetic constants (fate constants) is required to predict the transport and transformation of these chemicals. Examples of processes for which it is important to know the values of the fate constants are hydrolysis, sorption, biotransformation, photolysis, oxidation, volatilization, and water solubility.

Constants will be required for large numbers of chemicals. For example, approximately 1600 new chemicals or formulations are submitted to EPA's Office of Toxic Substances (OTS) each year for premanufacturing review and approximately 75 000 chemicals are potential candidates for review under the OTS existing chemicals program. Risk assessments are also made under various programs throughout EPA's offices. Relatively few of the needed constants have been published, and many of the published constants are of questionable reliability or applicability.

A program was developed at EPA's Environmental Research Laboratory at Athens, Georgia, (ERL-Athens) to provide equilibrium and kinetic constants for chemicals whose environmental transport and transformation must be assessed. The program is divided into: (a) searching the literature for measured data, (b) postulating transformation pathways and products, (c) performing laboratory

measurements when measured data cannot be located and/or computational techniques are not available, and (d) estimating data using computational techniques. Literature searches and laboratory measurements are performed for any fate constant requested whereas postulating transformation pathways and products are currently performed for hydrolysis only. Other transformation processes will be considered as they are better understood.

Requests for fate data come primarily from within EPA; however, requests from outside the agency will be filled as resources permit. Emphasis is placed on quality control features to assure the reliability of the data. These include checking the Chemical Abstract Service Registry Number, confirming the chemical name, verifying the value in the original or primary publication, cross-checking all entries into an archival database and evaluating the reliability of the fate constant. Reliability ratings are assigned to each reported parameter value using an evaluation system that was developed at ERL-Athens.¹

The progressive escalation of the need for a cleaner environment necessitates more and more the use of environmental fate data in the prediction process of the fate of toxic substances in the environment. Unfortunately, not many fate data are published in the literature. It will be beyond the scope of this paper to list already published data; however, it is the objective of this paper to give the environmental community some insight into how to obtain environmental data.

The Search Process

Extensive literature searches are performed in an attempt to locate experimentally determined process constants. Many of the constants found in the literature have not been determined under environmentally realistic conditions. In addition, it is not uncommon to locate several values for a given process constant for a specific chemical and to find no measured values for other chemicals for which data are needed. Once a measured value has been found in the literature, an attempt is made to locate the primary reference—a process that can be frustrating. Locating the primary reference is quite important, however, because we must be certain that the value is true to ensure reliability.

The chemical literature contains many synonyms for the same chemical, thus complicating a search by chemical name. For instance, phenylamine may be listed as aminobenzene or aniline. The most reliable method of assuring that data developed in a search are for the chemical of interest is through the use of the Registry Number. Registry Numbers do not have a chemical significance but are assigned in sequential order as chemicals are entered into the Chemical Registry System for the first time. Once a chemical has been defined in the original chemical literature, a number is assigned that is unique to that chemical. CAS Registry Numbers are listed in the *Registry Handbook* published by the American Chemical Society.² Most databases storing data on chemicals permit searches by entering the Registry Number.

When a request for data is received, the correctness of the Registry Number and the chemical name are verified by consulting the *Registry Handbook*, the *TSCA*

Chemical Substance Inventory,³ or the American Chemical Society's database CAS Online.

The next step involves searching for the needed data in various publications that contain fate constants and physicochemical properties for large numbers of organic chemicals.⁴⁻¹⁵ Concurrently, searches are started in various databases, using the CAS Registry Number to identify the chemical. Besides the values themselves, the full primary reference citation must be reviewed. The citation is then obtained, a process that may take several weeks if the citation is not available readily. Finally, the primary citation is reviewed to ensure the correctness of the value(s). This verification is most important if data were obtained from secondary references. Experience has shown that errors in transfer of numbers or units are easily made and overlooked. When more than one literature value is found, plans call for ranking the values by applying evaluation criteria to determine the degree of confidence with which the value(s) can be used.¹

DATABASES CONSULTED

The quickest and least expensive way of accessing data is through a computerized database. It is important to remember, however, that data collected in a database are removed from the original report and that errors can be detected, therefore, only by consulting the original documentation. Databases that list environmental fate data will also, generally, give some of the experimental conditions that values were obtained under.

DIALOG (DIALOG Information Services, Inc., 3460 Hillview Avenue, Palo Alto, CA 94304) is the largest online database access system, having more than 200 separate databases. Unfortunately, DIALOG stores little information on rate constants of organic chemicals. It does, however, have extensive information on other physical constants.

CAS Online, a database operated by the American Chemical Society (Chemical Abstracts Service, Box 02228, Columbus, OH 43202), is accessed through STN International. STN International is a cooperative of database producers that has three service centers, one each in Europe, Japan, and the United States. CAS Online stores more than seven million citations from more than 14 000 scientific journals published in more than 150 countries. The user has access to bibliographic data, indexing terms, and abstracts. Ultimately, the user must obtain the referenced paper to get the needed data, however.

Chemical Information Systems (CIS) (Chemical Information Systems, Inc., 7215 York Road, Baltimore, MD 21212) is a database access system permitting access to more than 35 separate databases. Some of these databases store fate and toxicity information for organic chemicals.

The Syracuse Research Corporation (Merrill Lane, Syracuse, New York 13210) has developed a small cluster of databases storing environmental data. DATA-LOG is a bibliographic environmental fate database. CHEMFATE stores literature-derived data pertinent to the environmental fate of chemicals. BIOLOG is a bibliographic database containing information on microbial biodegradation

and toxicity of chemicals. Complete references can be extracted from the DATA-LOG file.

The Graphical Exposure Modeling System (GEMS) is an interactive computer system located on the VAX Cluster in the National Computer Center in Research Triangle Park, North Carolina, under management of EPA's Office of Toxic Substances. GEMS provides a simple interface to environmental modeling, physico-chemical property estimation, statistical analysis, and graphic display capabilities. GEMS provides some of the computational techniques referenced in Lyman *et al.*¹⁶ in a simplified mode for estimation purposes.

Quantitative Structure-Activity Relationships (QSAR) is an interactive chemical database and hazard assessment system designed to provide basic information for the evaluation of the fate and effects of chemicals in the environment. QSAR was developed jointly by the U.S. EPA Environmental Research Laboratory, Duluth, Minnesota, and Montana State University and provides some of the computational techniques referenced in Lyman *et al.*¹⁶ in a simplified mode for estimation purposes.

PATHWAY ANALYSIS

If broader interest in fate data is needed, a team of scientists meets to discuss the probable pathways of transformation for chemicals of interest. Currently, only transformation by hydrolysis is considered, but other processes such as chemical oxidation and microbial transformation will be considered as these processes are understood better. The methods used to arrive at the reaction products are based primarily on the team's experience with similar compounds, knowledge of the hydrolysis theory, and structure activity relationships. First, the compounds that have no hydrolyzable functional groups (NHFG) are identified, followed by those that have non-labile functional groups (NLFG). Although these molecules contain one or more heteroatoms, their hydrolysis half-lives will be greater than 50 years—if they react at all under normal environmental conditions. Second, the molecular structures of the compounds that will react are analyzed. The team decides whether the reaction will most likely occur by substitution or elimination. The potential products of hydrolysis are predicted including the probable stable product. Additional literature searches are conducted afterwards to find needed fate data for the intermediate products of hydrolysis. If the literature fails to provide the required data, the needed fate data are determined in the laboratory or computational techniques are applied to estimate them.

Figures 1-4 are examples of pathway analyses for 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, and lindane. The pathway is given for each chemical with the CAS Registry Number, the name, the chemical structure, and for the parent and intermediate products the alkaline (k_B) and/or neutral (k_N) rates of hydrolysis including half-lives and references. Rate constants have the units of per mole per year ($M^{-1}Y^{-1}$) and half-lives, $t_{1/2}$, are given in years (Y).

When reaction products cannot be predicted with acceptable certainty, laboratory experiments are conducted to produce the products and identify them by

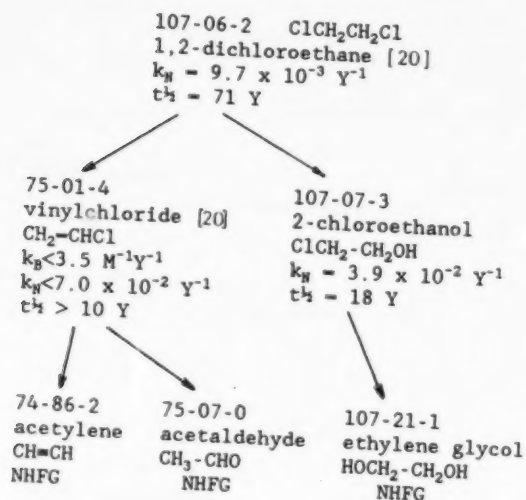


Figure 1 Pathway of hydrolysis of 1,2-dichloroethane. 1,2-Dichloroethane hydrolyzes to the fairly stable product vinyl chloride and to the final stable product ethylene glycol through the intermediate product 2-chloroethanol. Vinyl chloride may further hydrolyze to acetylene at alkaline pHs or to acetaldehyde at near neutral pH. Ethylene glycol is the main product at near neutral pH, and the reaction shifts to give vinyl chloride as the pH increases. Hydrogen chloride is formed in the process. (2-Chloroethanol data were obtained from J. J. Ellington, personal communication.)

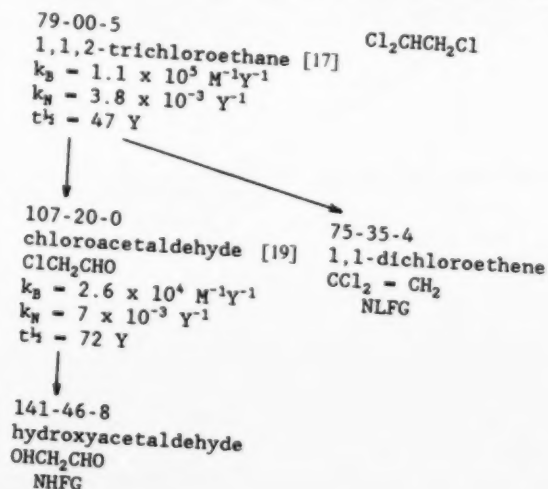


Figure 2 Pathway of hydrolysis of 1,1,2-trichloroethane. 1,1,2-Trichloroethane hydrolyzes to the final stable product hydroxyacetaldehyde through the intermediate product chloroacetaldehyde and to the final stable product 1,1-dichloroethene. Hydrogen chloride is formed in the process.

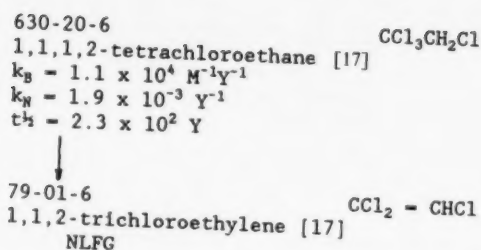


Figure 3 Pathway of hydrolysis of 1,1,1,2-tetrachloroethane. 1,1,1,2-Tetrachloroethane hydrolyzes to the final product, 1,1,2-trichloroethylene. Hydrogen chloride is formed in the process.

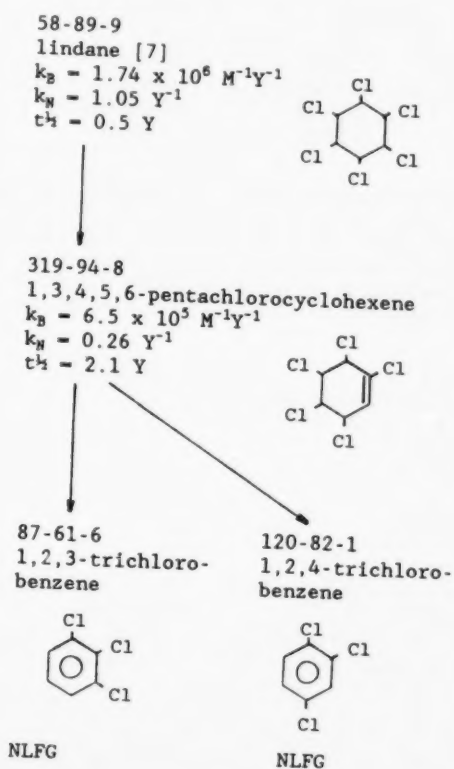


Figure 4 Pathway of hydrolysis of lindane. Lindane hydrolyzes through the intermediate product, 1,3,4,5,6-pentachlorocyclohexene, to the final stable products, 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene. Hydrogen chloride is formed in the process. (Pentachlorocyclohexene data were obtained from J. J. Ellington, personal communication.)

spectroscopic analyses. Because risk should be assessed for the residual chemical in an environment and not for the parent compound or reactive intermediate products, an expanded postulation process is an important goal to achieve. Moreover, it is important to remember that different fate processes can result in different residual chemicals in a particular environment. Again, it is the residual chemical for which risk should be assessed.

LABORATORY-MEASURED DATA

Part of ERL-Athens' mission is to determine the occurrence of unsuspected organic pollutants in the aquatic environment and develop and apply techniques to measure physical, chemical, and microbial transformation and equilibrium constants for use in assessment models.

A protocol is established for each process to assure compatibility with future experiments. These protocols describe the entire experimental scheme including planning, sample requirements, experimental set up and chemical analysis, handling of data, and quality assurance. Only established analytical methods are applied and the purity and identity of the chemical are determined by spectroscopic means. The name on the label of the chemical's container is not a proof of its identity. Standard reference compounds (SRCs) are tested with each experiment. SRCs are compounds that are used as quality assurance standards and as references in inter-laboratory generation of data. The value of the process constant(s) has been well established for an SRC and serves as baseline information for evaluating all experimental techniques and all aspects of quality assurance. Because the SRC is taken through the entire experimental scheme, parallel to the test chemical, its result will tell the experimenter how much confidence he/she can have in all phases of the experiment.

The expertise and procedures developed at ERL-Athens in measuring rate and equilibrium constants assure a quality value of known accuracy and precision determined under environmentally realistic conditions.

ESTIMATED DATA

The increased necessity for assessing health and ecological risk from pollutant exposure has created a tremendous need for fate processes constants. The inherent complexity in measuring physical and chemical properties (especially of hydrophobic chemicals) makes the measurement process a very difficult and, therefore, expensive one. Even if we ignore the prohibitively large cost of the measurement process, we will never be able to satisfy the need for data experimentally because of time constraints. For these reasons, we need reliable computational techniques to estimate physical and chemical properties. Moreover, computational techniques will generate values at a fraction of measurement costs and will eventually satisfy the need for much of the required data.

The largest compilation of chemical property estimation methods was made by

Lyman *et al.*¹⁶ Most methods are based on property-reactivity correlations and allow estimation of a number of constants, but relationships often hold only within limited families of chemicals. The rate of aqueous photolysis and the rate of biotransformation cannot be estimated quantitatively at present. Sorption coefficients, water solubilities and volatilization rates can be estimated, however, even though other properties may have to be known to do so. The rate of hydrolysis can be estimated through the application of linear free energy relationships (LFER). Unfortunately, the very limited availability of LFER data makes it practically impossible to do any worthwhile predictions.

A most promising computer technology for predicting chemical reactivity is the prototype computer expert system being developed by scientists at ERL-Athens and the University of Georgia. The system uses computational algorithms based on fundamental chemical structure theory, which allows estimation of values for any parameter that depends upon molecular structure. Although the system is presently capable of predicting only sunlight absorption spectra and ionization constants, with remarkable accuracy, the capability of predicting reaction rate constants is being developed.

CONCLUSION

In assessing potential risk posed by chemicals in the ambient environment, it is essential that reliable fate constants be available. The program at ERL-Athens provides reliable constants by developing the expertise to locate, measure, estimate, and evaluate fate data. The postulation of transformation pathways and products, which is at present being performed for chemical hydrolysis only, will be expanded to include other important transformation processes such as photolysis, chemical oxidation, and biotransformation. The expansion is most important because risk should be assessed for the "persistent" residual chemical(s) and not for the "transient" parent compound or intermediate products alone.

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